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In situ preparation of TiB_2 reinforced Al base composite

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Abstract—*In situ* formation of Al-TiB_2 metal matrix composite has been successfully fabricated through an exothermic reaction process. The base alloy used in the present investigation was Al–4 wt% Cu. It was first melted at 850°C. After that, two types of salts, namely, K_2TiF_6 and KBF_4 were added into the molten Al alloy by stirring. An exothermic reaction between the two salts and molten Al took place to form *in situ* TiB_2 particulates in the molten Al alloy. The exothermic reaction period was varied from a minimum 5 min to a maximum 35 min to investigate the relationship between the degree of reaction, the growth behaviour and the microstructures of TiB_2. After the reaction, the composite was cast into rods of 25 mm diameter. Both X-ray diffraction measurement and scanning electron microscope analysis revealed the formation of TiB_2. The amount of TiB_2 particulates increased when the exothermic reaction period was prolonged. Its microstructure was examined under optical and scanning electron microscopes.

Keywords: Metal matrix composites; *in situ* TiB_2; microstructures; grain refinement.

1. INTRODUCTION

Materials can be strengthened by the introduction of secondary phases such as ceramic reinforcement in the size range suitable for Orowan strengthening mechanism. Orowan strengthening requires very fine reinforcement particulates homogeneously dispersed within the matrix. However, discontinuous reinforcements are rarely available in a size less than 500 nm. In addition, even if a suitable size reinforcement is available, it is very difficult to disperse the reinforcement uniformly using either the powder blending or the casting techniques [1].

Wettability between ceramic particulates and metal matrix materials is a major problem in the fabrication of metal matrix composites. To overcome this problem and hence to increase the bonding strength between the particulates and the matrix, the reaction process has received a new attention as a better way to produce *in situ* ceramic particulates in the fabrication of Al-based [2–4], Ti-based [5], Ni-based [6] and other type-based [7] metal matrix composites. Three main types of *in situ* ceramics have been synthesized, namely, Ti-B, Ti-C and B-C types. The resultant self-reinforced metal matrix material appears to have advantages over other reinforced composites because of the unique ability to tailor their microstructure to give better combination of mechanical and thermal properties. Especially attractive is technology that results in families of materials with controllable properties and microstructures.

Most of the studies reported so far are related to fabrication and mechanical properties of silicon carbide or alumina-reinforced Al alloy composites. Information on the synthesis of composites dealing with *in situ* TiB_2 reinforcement is, however, very limited.

The present study focuses on the synthesis of *in situ* MMC and on the effects of processing parameters on *in situ* formed TiB_2 reinforcement and its microstructures.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

In the present investigation, 99.9% pure Al and Cu elements with a composition of Al–4 wt% Cu were used as the base metal. Two types of slats, namely, K_2TiF_6 and KBF_4 were employed to synthesize the TiB_2 reinforcement.

2.2. Processing

Base metal of Al alloy was first melted at 850°C. After melting of the base metal, the two salts were gradually added into the molten Al alloy in the atomic ratio in accordance with Ti/2B by using stirring method. Two types of stirrers were used: they were steel stirrers coated with ZrO and graphite stirrers. Chemical reaction between the two salts and the molten Al took place to form *in situ* TiB_2 particulates. The period of chemical reaction was varied in steps from 5 min to 35 min at 850°C to investigate the relationship between degree of reaction, the growth behaviour and the microstructures of TiB_2. After the reaction, stirring was stopped for a while to let the slug float to the top of the melt. Then, the composite was cast into rods of 25 mm diameter.

2.3. Microstructure measurement

Microstructures of the resultant materials were examined under optical and scanning electron microscopes (SEM). Formation of new phases in the present work was monitored using a Philips PW1729 X-ray diffractometer with Cu Kα radiation operated at 30 kV and 20 mA. Grain size was measured in accordance with ASTM E112-88 standard [8] and measured by using a Quantimet.

3. RESULTS AND DISCUSSION

3.1. In situ *formation of TiB_2 ceramic particulates*

The formation of TiB_2 is an exothermic process where the chemical reaction occurs according to the following sequence [9]:

$$K_2TiF_6 + Al \Rightarrow TiAl_3 + KAlF_4 + K_3AlF_6, \quad (1)$$

$$KBF_4 + Al \Rightarrow AlB_2 + KAlF_4, \quad (2)$$

and

$$AlB_2 + TiAl_3 \Rightarrow TiB_2 + Al. \quad (3)$$

It is believed that the chemical reaction is similar to that in grain refinement of Al using Al-Ti-B master alloy. The initial divergent reactions produce $TiAl_3$ and AlB_2 followed by the intermediate phases of $(Ti, Al)B_2$ [10]. As the actual chemical reactions are more complicated than those depicted above, the exact reaction sequence is difficult to define.

Figure 1 shows the X-ray diffraction (XRD) patterns of the MMC formed *in situ* after a reaction time of 35 min. The formation of TiB_2 has been confirmed by the presence of TiB_2 peaks. For short reaction time, TiB_2 peaks are difficult to observe since the volume fraction of *in situ* TiB_2 is very low and the strongest TiB_2 XRD peak overlaps with the (111) plane of Al. With the increase in reaction duration, more TiB_2 particulates were formed *in situ*. Therefore, the intensity of the TiB_2 XRD peaks increased. It is noted that there are some XRD peaks near the Al (111) peak. According to the diffraction angles of the peaks and the formation process of TiB_2 from Ti and B, they are believed to be caused by the presence of $TiAl_3$ in this MMC. From the reaction sequences of equations (1) to (3), it is known that, besides formation of TiB_2 within molten Al, another two salts, namely $KAlF_4$ and K_3AlF_6,

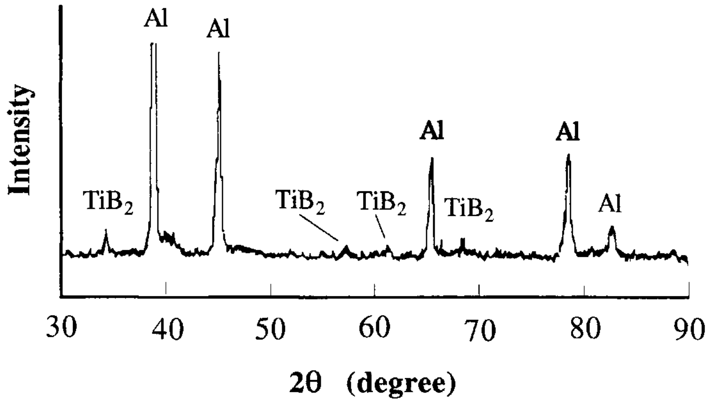
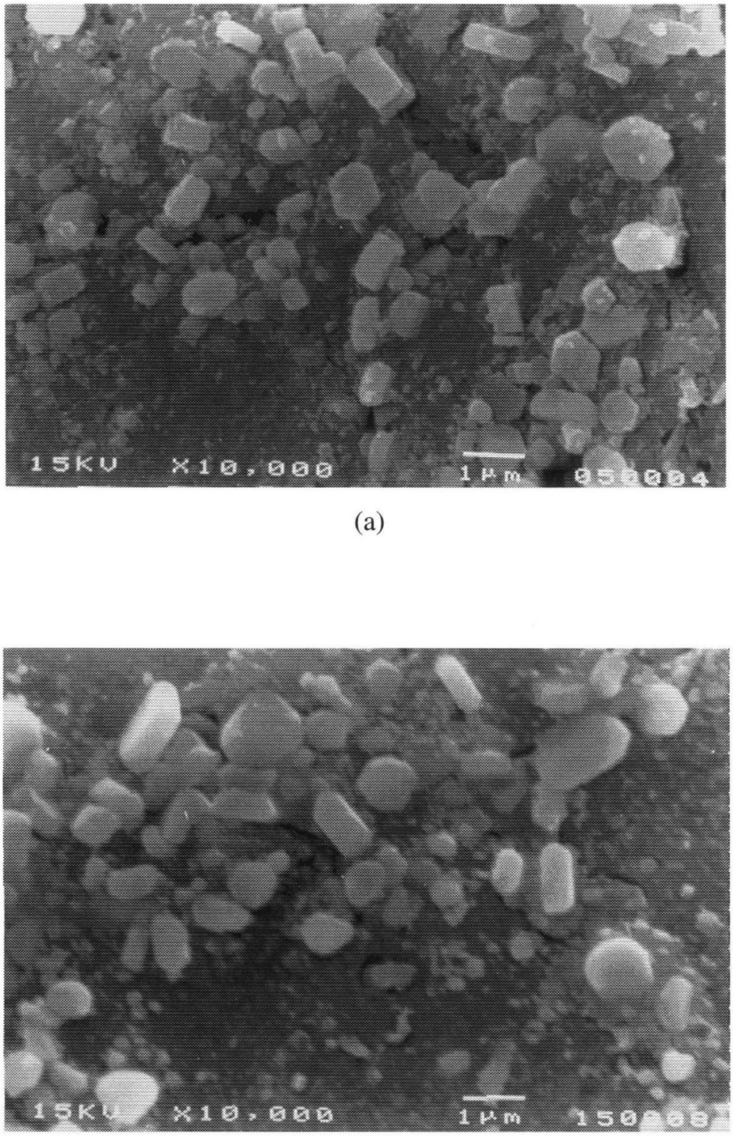


Figure 1. X-ray diffraction patterns of Al-based composite prepared *in situ*.

were formed during the chemical reaction. Since the densities of these salts are lower than that of the melt, they floated on the top of the melt as a slug after stirring ceased.

3.2. Microstructure

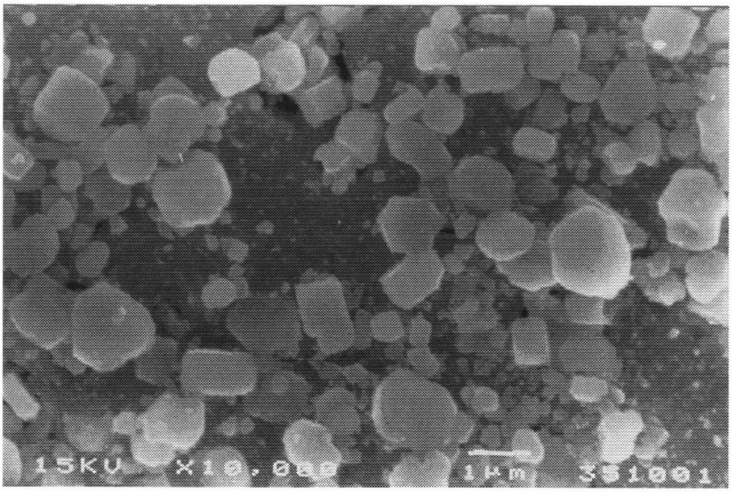
Figures 2 (a) to (c) show the microstructures of the MMC after different reaction



(a)

(b)

Figure 2. *In situ* formation of TiB_2 reinforcement at different reaction times of: (a) 5 min, (b) 25 min, and (c) 35 min.



(c)

Figure 2. (Continued).

durations. It was observed that TiB_2 began to form after just 5 min of chemical reaction, as evident from the hexagonal shape particulates located mainly along grain boundaries (Fig. 2(a)). However, owing to short reaction time and a relatively low reaction temperature, complete reaction was not achieved, as indicated by residual salts that could still be found after casting. Consequently, only a small amount of TiB_2 particulates has been observed. Particle size of the TiB_2 at this stage was measured to be in the range of about 0.5 μm in diameter although some of them were much smaller. Since the chemical reaction took place entirely in the molten Al, there was no oxidation layer on the surfaces of the TiB_2 particles. The latter was observed to be homogeneously distributed around the grain boundaries and interdendritic region. No large agglomerations of TiB_2 or porosity could be noticed. From microstructural observation, some very fine particles with Ti-rich composition could be seen within the grains. According to a study on the grain refinement, when excess Ti is present, most of the TiB_2 particulates will be located within the grains [13]. More detailed transmission electron microscopy (TEM) study uncovered the presence of TiB_2 particulates actually within the $TiAl_3$ [14].

Chemical reaction of the salts became more complete when the reaction time was increased. After 35 min of chemical reaction, TiB_2 had grown to a mean size of about 1 μm where a clear hexagonal shape could be observed (Fig. 2(b) and (c)). The particle size distribution of TiB_2 is given in Fig. 3, which shows a very slow increase in the size of TiB_2 particulates.

It is noted that as reaction time is increased, besides the increase in the amount of TiB_2, grain size of the matrix changes as shown in Figs 4(a) to (d). In general, the change in grain size can be divided into two stages. At the early stage (Figs 4(a)–(c)), grain size decreased dramatically with the increase in reaction time. At the later

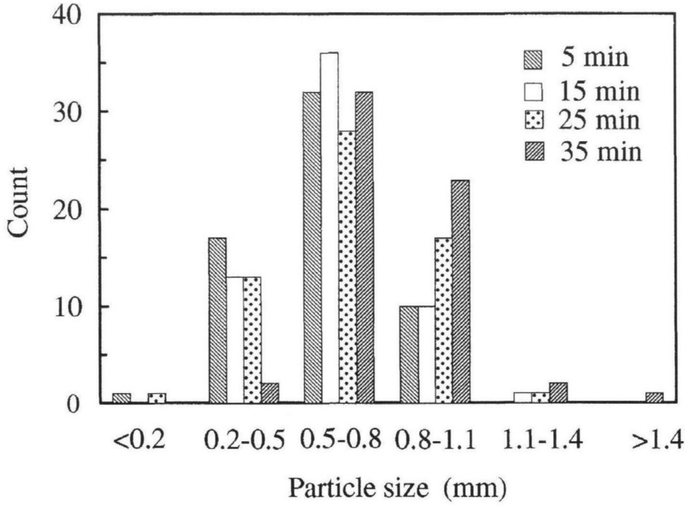
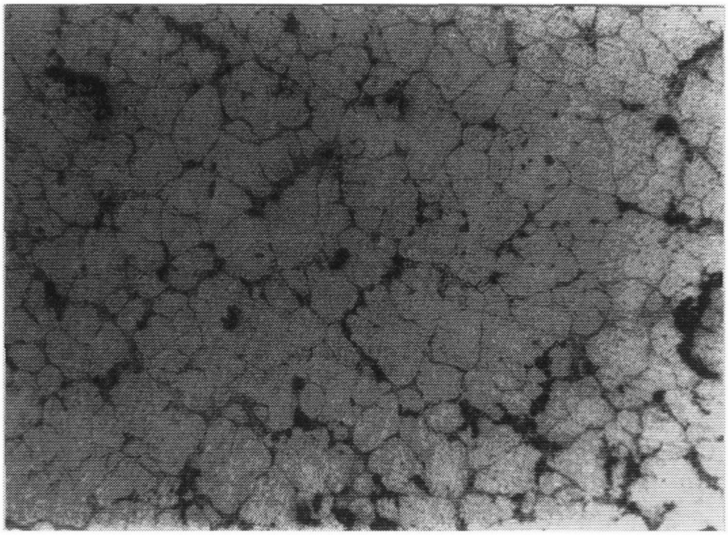


Figure 3. Distribution of TiB_2 particle size at different reaction times.

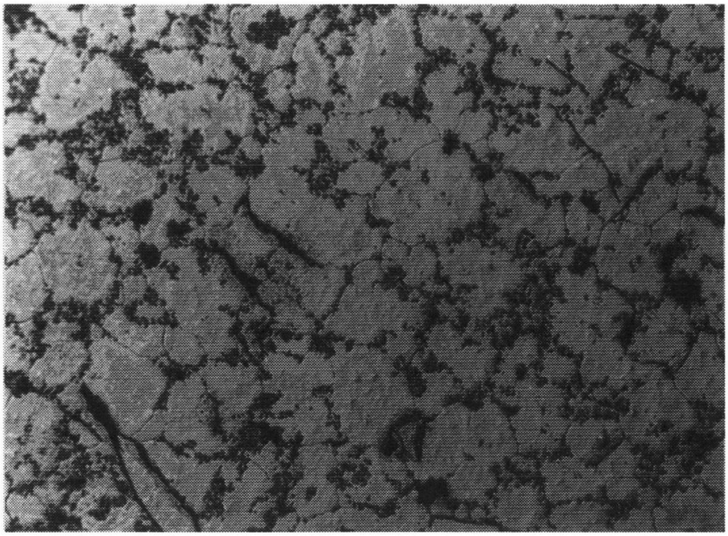
stage of the reaction (Fig. 4(d)), grain size increased slightly. The measurement of grain size is given in Fig. 5. It is known that when the Ti/B ratio corresponds to the stoichiometric TiB_2 phase, the addition of Ti-B into Al does not cause grain refinement when added. Only when Ti is present in excess of the TiB_2 ratio can grain refinement be achieved. The degree of grain refinement depends very much on the morphology of the $TiAl_3$ intermetallic compound. Arnberg *et al.* [11] have observed the formation of TiB_2 and AlB_2 when grain refinement of Al was induced by addition of Al-Ti-B type master alloy.

Crystals with compositions between the two pure binaries could be formed initially under the appropriate conditions by adding the alloying elements. However, holding the alloy at 750°C for a long time resulted in a transition towards the TiB_2 structure. This observation is in agreement with thermodynamic calculations [12]. TiB_2 is the stable form of boride in Al. Mohanty and Gruzleski [13] introduced TiB_2 particulates into molten Al. The particulate number density was found to be approximately $43/cm^2$ before remelting. This density remained almost the same after remelting and holding for a period of 6 h. No significant change in particle size or chemistry was observed. Electron probe analysis indicated no trace of Al within these particulates, confirming that TiB_2 particulates once introduced into the Al are stable.

According to the present observations, it can therefore be concluded that although the ratio of Ti/B from the two kinds of salts corresponded to TiB_2, the reaction depicted in equation (1) was much faster than that in equation (2), and the reactions in equations (1) and (2) were faster than that in equation (3). Hence, the presence of $TiAl_3$ gave rise to the effect of grain refinement. Another possibility of grain refinement may be due to the short reaction time. Because of this, there was not enough time for the complete reaction indicated by equation (3) to take place. On the other hand, with long holding time at 850°C, most of the Ti in the form of $TiAl_3$ intermetallic compound was found to decompose into a stable TiB_2 phase. The



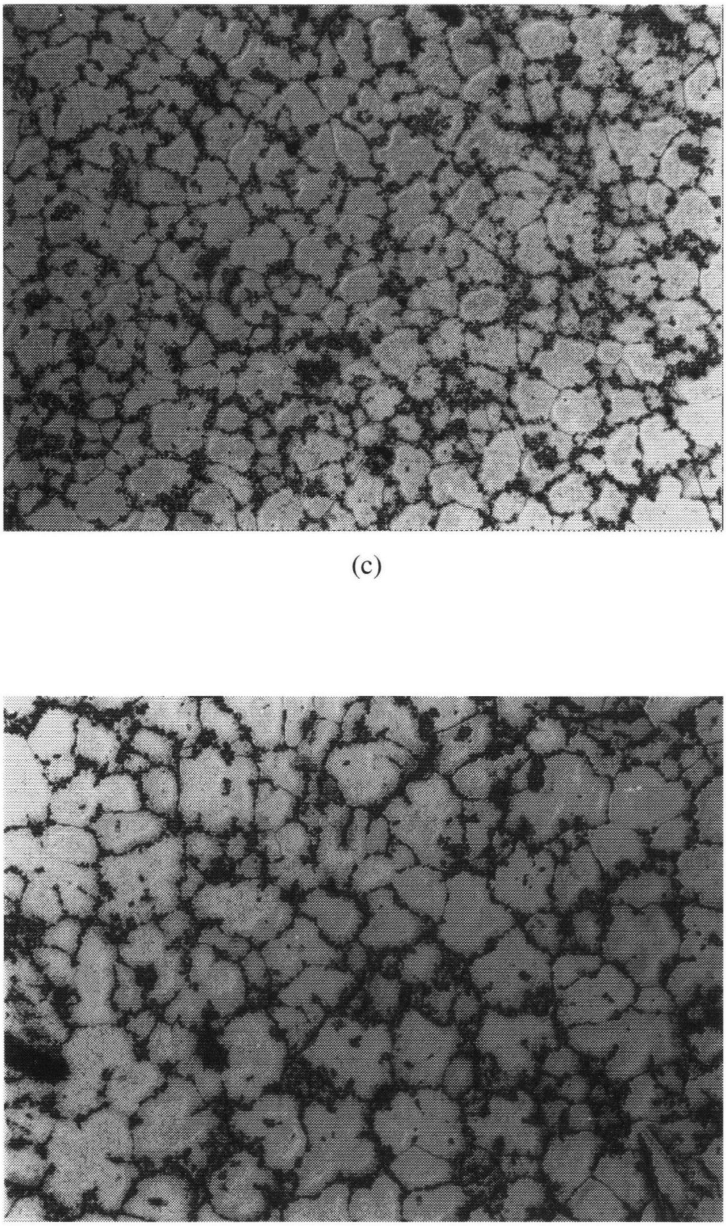
(a)



(b)

Figure 4. Optical microscopic observation of *in situ* MMC at different reaction times of: (a) 5 min, (b) 15 min, (c) 25 min and (d) 35 min.

decomposition of $TiAl_3$ led to a reduction in the numbers of divergent sites. The result is that there was less effect of grain refinement from addition of Ti. This explains why grain refinement took place followed by an increase in grain size.



(c)

(d)

Figure 4. (Continued).

Selection of materials for a stirrer is also a key factor in the processing of *in situ* MMCs. Because Ti is very reactive with other materials at high temperature, TiFe and Al_3Fe intermetallic compounds can form although the iron stirrers have been coated

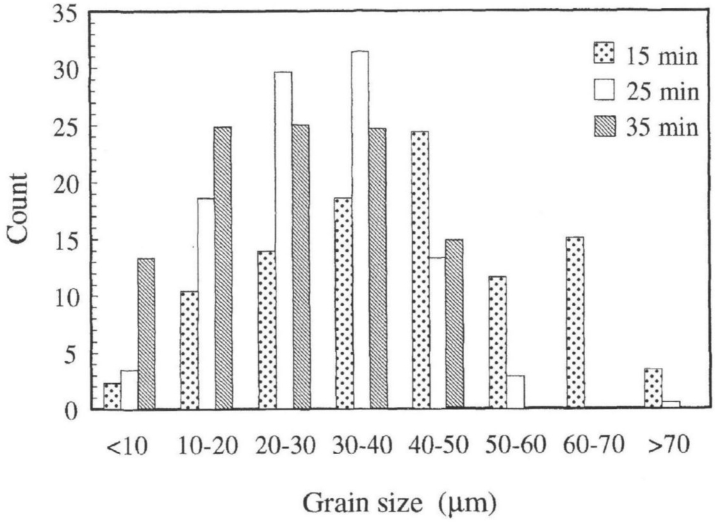


Figure 5. Distribution of grain size after different reaction times.

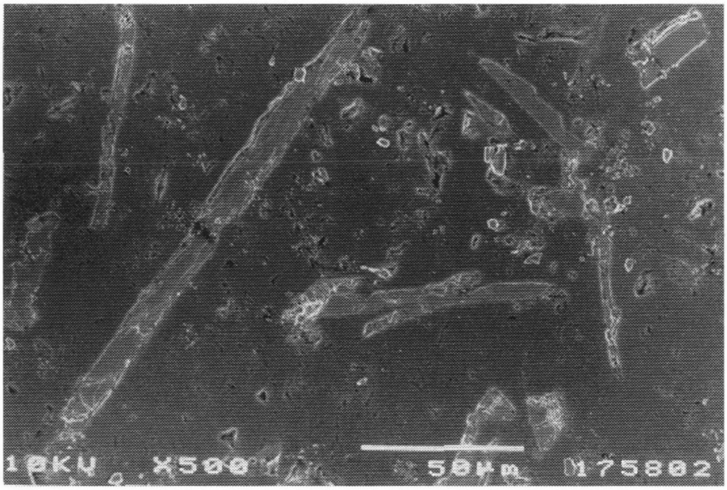


Figure 6. Microstructure of the MMC formed *in situ* using iron stirrer.

with ZrO. Figure 6 shows the microstructure of the MMC formed *in situ* using an iron stirrer. The high Fe concentration was detected in the areas with needle shape. EDX examination shows that the chemical compositions correspond to TiFe and Al_3Fe. No needle shape microstructure was observed if the iron stirrer coated with ZrO was used for the processing of matrix material.

4. CONCLUSIONS

(a) *In situ* TiB_2 has been successfully synthesized via an exothermic reaction between Ti and B salts. The formation of TiB_2 particulates with the size in the range of 0.5 to a maximum 2 μm have been confirmed by X-ray diffraction patterns.

(b) The volume fraction of *in situ* TiB_2 was observed to increase with reaction time. This observation indicates that the chemical reaction was not complete even after a holding time of 35 min at 850°C.

(c) Change in the grain size was observed as a function of chemical reaction duration. The grain size shows a decrease with the increase in the reaction duration at beginning of reaction. The grain size, however, shows a slight increase with a longer reaction duration. Because the grain refinement effect is due mainly to the presence of $TiAl_3$, it is believed that the amount of $TiAl_3$ increases at the beginning of reaction and it decreases at a later stage of reaction. Due to the presence of $TiAl_3$, some very small TiB_2 particulates exist within grains. Those small TiB_2 particulates were surrounded by a $TiAl_3$ layer which was a dominating factor for the grain refinement.

(d) The present study shows that *in situ* formation of reinforcement is a better method of fabricating metal matrix composites than conventional casting. Reinforcement with very small particle size can homogeneously be incorporated into the matrix.

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